PATENT SPECIFICATION

738,538

Date of Application and filing Complete Specification: Aug. 19, 1953.
No. 22900/53.
Application made in United States of America on Sept. 16, 1952.
Complete Specification Published: Oct. 12, 1955.

Index at acceptance:—Class 91, D2(H:N:W).

COMPLETE SPECIFICATION

Detergent Compositions

We, GENERAL ANILINE & FILM CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 230, Park Avenue, New York, County and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergent compositions, and more particularly to detergent compositions of the polyoxyalkylene type, and processes for employing same.

It is an object of this invention to provide detergent compositions of the aforementioned type having improved foaming, foam stable and detergent properties. It is another object to provide a washing process employing such improved compositions. Other objects and advantages will appear as the description proceeds.

The aforementioned objects are obtained by the present invention which involves the provision of a detergent composition comprising (1) a water soluble chloride, sulfate, nitrate, bromide or acetate of a polyvalent metal and (2) a compound of the formula:

$$R—O(CH_2—\underset{\displaystyle X}{\underset{|}{C}}H—O)_n—SO_3—M$$

in which R is a hydrocarbon radical containing at least 10 carbon atoms selected from the group consisting of alkyl radicals containing a plurality of branched chains, and alkylaryl radicals. X is selected from the group consisting of H and CH_3, M is a monovalent water solubilizing cation, and n is from 1 to 8.

The compositions of this invention have been found to have improved foaming and foam-stable properties in addition to increased rates of detergency and detergent efficiencies with respect to compositions containing the same polyoxyalkylene compounds but without the polyvalent metal salts. The mechanism whereby the improved results are obtained is not thoroughly understood, but it is apparent that some synergistic effect is involved. This should be apparent from the fact that the water soluble salts of polyvalent metals, generally speaking, do not per se have any foaming or detergent properties. It is, therefore, indeed surprising that the addition of these water soluble salts of polyvalent metals to polyoxyalkylene compounds of the above-mentioned type improves the foaming and detergent properties of such compounds to the remarkable extent described herein.

Polyoxyalkylene compounds of the above-mentioned type in which R is an alkyl radical containing a plurality of branched chains, and their process of manufacture, are disclosed and claimed in copending Application No. 32457/52, filed December 22, 1952 (Serial No. 719,445). In general, such compounds may be derived from branched chain primary aliphatic alcohols such as: 2,4,5,5,7-pentamethyl-1-octanol, 2,3,5,7-tetramethyl-1-nonanol, 3,5-diethyl-1-octanol, 2,4,7-trimethyl-1-nonanol, 2,4,5,6,8-pentamethyl-1-nonanol, 2,6,7-trimethyl - 3 - ethyl-1-octanol, 2,4,6,8 - tetramethyl - 1 - nonanol, 2,3,5-trimethyl-4,7-diethyl - 1 - octanol, 2,3,5,6-tetramethyl-5,7-diethyl - 1 - octanol, 3,5-dimethyl-4,6-diethyl - 1 - heptanol, 3,4,5-trimethyl-4,6-diethyl-1-heptanol, 2-ethyl-3,5,7-trimethyl-1-octanol, 2-ethyl-4,6-dimethyl-1-octanol, 4-butyl-2-methyl-1-octanol, 2,5,7,7-tetramethyl-1-octanol, 3,5,7,7-tetramethyl-1-octanol, 2,5-diethyl-3,7-dimethyl-1-octanol, and 2,5,7,9-tetramethyl-1-decanol. Preferably alcohols are used which are prepared by the catalytic reaction of an olefin such as tripropylene, tetrapropylene, pentapropylene, triisobutylene, tetraisobutylene, tributene, 4,6,8-trimethyl-1-nonene, 4,6,8-trimethyl - 2 - nonene, mixed propene-butene polymers, 5,7,7-trimethyl-1-octene, 3,5,7-trimethyl - 1 - heptene, and 2,4,6,6,8-pentamethyl-1-nonene, with carbon monoxide and hydrogen to form an aldehyde followed by catalytic reduction of this aldehyde to an alcohol. This two-stage process is

known as the oxo process. Alcohols produced by the oxo process may be designated as oxo alcohols. Thus the oxo tridecyl alcohol mentioned hereinafter and in the claims is the $C_{13}H_{27}OH$ polybranched chain primary aliphatic alcohol prepared from tetrapropylene by the oxo process.

The above-mentioned polyoxyalkylene compounds of the type in which R is an alkylaryl radical and their process of manufacture are disclosed in United States Patent No. 2,203,883. Such compounds may be derived from alkylated aromatic hydroxy compounds such as p-n-butylphenol, amylcresol, diisobutylphenol, diamylphenol, isohexylnaphthol, oleylphenol, isododecylphenol, isooctylresorcinol, nonylphenol, dinonylphenol, isooctylphenol, isooctyl-8-naphthol, isohexylxylenol, n-octadecylphenol, and the like. These preferred alkylated aromatic hydroxy compounds all contain an aryl radical substituted by an alkyl group of at least four carbon atoms.

The above-mentioned alcohols and phenols are, in general, condensed under proper conditions with the required number of moles of ethylene oxide or propylene oxide, the condensation products thus obtained esterified with sulfuric acid or a suitable sulfuric acid derivative, and the resulting sulfuric acid esters neutralized to produce the monovalent water soluble salts thereof. General methods for carrying out the oxyalkylation reaction, the esterification and the salt formation in producing the polyoxyalkylene compounds employed in this invention are illustrated in British Patents Nos. 380,431 and 380,851 and United States Patents 2,174,761 and 2,167,326.

The invention is particularly effective when employing the ammonium, sodium, potassium, alkylammonium or hydroxyalkylammonium, salts of the sulfuric acid esters of polyoxyalkylene compounds of the above-mentioned type containing from 1 to 8, and preferably 1 to 6 polyoxyalkylene groups. Compounds containing 2—4 polyoxyalkylene groups are particularly preferred. Outstanding results are obtained when the compound is derived from oxotridecyl alcohol and ethylene oxide.

The water soluble salts of polyvalent metals which may be employed are, for example, the chlorides, sulphates, nitrates, bromides and acetates of magnesium, calcium, aluminum and iron or mixtures thereof. In some cases, it is preferable to use the hydrates of the aforementioned salts. Because of the required water solubility and other characteristics, the magnesium and calcium chlorides are preferred. These salts or mixtures thereof are employed in proportions of about 5 to 50% and preferably from about 10 to 45% by weight of the polyoxyalkylene compound.

When employed for detergent purposes, relatively small amounts of the composition of this invention are required to be dissolved in aqueous solution. Thus a solution containing .05% of the active polyoxyalkylene compound is sufficient to provide improved detergent and foam producing properties, although larger or smaller amounts may be employed when desired. The optimum amount in any particular instance will, of course, be readily determinable by a worker skilled in the art. Concentrates may be prepared for market in liquid or powdered form, or the like. The outstanding properties of the compositions of this invention are especially noticeable when employed in deionized, distilled or very soft water.

The examples set forth in the tables hereinafter are illustrative of the present invention and are not to be regarded as limitative.

In Table 1 the hand dishwashing test consists essentially of washing dishes of 9" diameter, spread with 3 g. of a melted mixture of 80 parts hydrogenated cottonseed oil, 20 parts ordinary bread flour, and 0.5 parts graphite in oil. The number of dishes washed before the foam disappears is considered to be the end point for this test. The time required to wash 8 dishes is also an important criterion of effectiveness in this test.

The foam stability test of Table 2 is carried out by preparing a detergent solution in a jar and then adding clean water through a funnel to the solution and measuring the foam height at definite time intervals.

The examples of compositions which do not contain polyvalent metal salts are included in the Tables merely for comparative purposes to illustrate the improvements attained by the present invention.

TABLE 1.

HAND DISHWASHING TEST

Example	Product (0.05% active material is distilled water)	No. of Soiled Dishes To Break Foam	Time to Wash 8 dishes (min.)
1.	Iso-octylphenol + 4 moles E.O. (sulfate, Na^+ salt)	6	5.7
2.	90% Iso-octylphenol + 4 moles E.O. (sulfate, Na^+ salt) 6% $CaCl_2$ 4% $MgCl_2$	10	4.0
3.	70% Iso-octylphenol + 4 moles E.O. (sulfate, Na^+ salt) 18% $CaCl_2$ 12% $MgCl_2$	18	
4.	Nonylphenol + 4 moles E.O. (sulfate, NH^+_4 salt)	5	8' + *
5.	50% Nonylphenol + 4 moles E.O. (sulfate, NH^+_4 salt) 6% $CaCl_2$ 4% $MgCl_2$	18	3.4
6.	80% Nonylphenol + 4 moles E.O. (sulfate, NH^+_4 salt) 20% $MgCl_2.6H_2O$	18	
7.	70% Nanylphenol + 4 moles E.O. (sulfate, NH^+_4 salt) 18% $CaCl_2$ 12% $MgCl_2$	18	
8.	Oxo tridecyl alc. + 2 moles E.O. (sulfate, NH^+_4 salt)	1	6' + for 5 dishes **
9.	90% Oxo tridecyl alc. + 2 moles E.O. (sulfate, NH^+_4 salt) 6% $CaCl_2$ 4% $MgCl_2$	24	4.0
10.	70% Oxo tridecyl alc. + 2 moles E.O. (sulfate, NH^+_4 salt) 18% $CaCl_2$ 12% $MgCl_2$	34	
11.	80% Oxo tridecyl alc. + 2 moles E.O. (sulfate, NH^+_4 salt) 20% $MgCl_2.6H_2O$	25	
12.	70% Nonylphenol + 4 moles Pr.O. (sulfate, NH^+_4 salt)	3	
13.	70% Nonylphenol + 4 moles Pr.O. (sulfate, NH^+_4 salt) 18% $CaCl_2$ 12% $MgCl_2$	6	

* (8th dish not clean)

** (5th dish not clean)

E.O. = ethylene oxide.

Pr.O. = propylene oxide.

TABLE 2.

FOAM STABILITY TEST.

	Product (0.05% active material in distilled water)	Ht. of Foam, Cm. at the end of 0 Min.	2 Min.	5 Min.
14.	Oxo tridecyl alc. + 2 moles E.O. (sulfate, NH^+_4 salt)	10.5	4.0	2.0
	80% Oxotridecyl alc. + 2 moles E.O. (sulfate, NH^+_4 salt) plus 20% of:			
15.	Calcium chloride	11.5	9.5	9.0
16.	Magnesium sulfate	11.5	8.5	8.0
17.	Calcium acetate	11.5	10.0	9.5
18.	Aluminum sulfate	12.0	10.0	9.0
19.	Ferrous sulfate	13.0	10.0	7.5
20.	Sodium sulfate	10.5	4.0	2.0
21.	Sodium chloride	10.0	4.0	2.0
22.	Sodium tripolyphosphate	12.0	5.0	2.0
23.	Lauryl ethanolamide	12.5	3.0	2.0
24.	Nonylphenol + 4 moles E.O. (sulfate, NH^+_4 salt)	11.0	6.5	4.0
25.	90% Nonylphenol + 4 moles E.O. (sulfate, NH^+_4 salt) 6% $CaCl_2$ 4% $MgCl_2$	10.0	8.5	7.5

The results summarized in Tables 1 and 2 clearly illustrate the unusual degree of improvement in foaming, foam stability and detergency obtained by the use of the present invention.

What we claim is:—

1. A composition comprising (i) a water soluble chloride, sulfate, nitrate, bromide or acetate of a polyvalent metal and (ii) a compound of the formula:

$$R—O(CH_2—\underset{\displaystyle X}{\underset{|}{CH}}O)_n—SO_3—M$$

in which R is a hydrocarbon radical containing at least 10 carbon atoms selected from the group consisting of alkyl radicals containing a plurality of branched chains, and alkylaryl radicals, X is selected from the group consisting of H and CH_3, M is a monovalent water-solubilizing cation, and n is from 1 to 8.

2. A composition according to claim 1 containing about 5 to 50% of said salt (1) by weight of said compound (2).

3. A composition according to claims 1 or 2 wherein said polyvalent metal is magnesium, calcium, aluminum or iron.

4. A composition according to any of the preceding claims wherein said salt (1) is magnesium chloride.

5. A composition according to any of claims 1 to 3, wherein (1) is a mixture of magnesium chloride and calcium chloride.

6. A composition according to any of the preceding claims wherein said compound (2) is derived from the condensation product of from 1 to 8 moles of ethylene oxide with 1 mole of a primary aliphatic alcohol of at least 10 carbon atoms containing a plurality of branched chains.

7. A composition according to claim 6 wherein said alcohol is OXO tridecyl alcohol.

8. A composition according to any of claims 1 to 5 wherein said compound (2) is derived from the condensation product of from 1 to 8 moles of ethylene oxide with 1 mole of a phenol substituted by an alkyl group of at least 4 carbon atoms.

9. A composition according to claim 8 wherein said phenol is isooctyl phenol.

10. A composition according to claim 8 wherein said phenol is nonyl phenol.

11. A composition in accordance with this invention substantially as described in the foregoing specification or in Examples 2, 3, 5, 6, 7, 9, 10, 11, 13, 15, 16, 17, 18, 19 or 25.

12. A washing process comprising contacting soiled objects with a composition comprising (1) a water soluble chloride, sulfate, nitrate, bromide or acetate of a polyvalent metal and (2) a compound of the formula:

$$R—O(CH_2—\underset{\displaystyle X}{\underset{|}{CH}}O)_n—SO_3—M$$

in which R is a hydrocarbon radical containing at least 10 carbon atoms selected from the group consisting of alkyl radicals containing a plurality of branched chains, and alkylaryl radicals, X is selected from the group con-

sisting of H and CH_3, M is a monovalent water-solubilizing cation, and n is from 1 to 8.

13. A process according to claim 12 wherein said polyvalent metal salt is magnesium, calcium, aluminum or iron.

14. A process according to claims 12 or 13 wherein R is derived from Oxo tridecyl alcohol, iso-octyl phenol, or nonyl phenol.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1955.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.